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14. ABSTRACT The principal objective of the research is to develop surrogates that will reproduce selected aspects of combustion of JP-8 in laminar non-premixed and premixed flows. Surrogates are mixtures of hydrocarbon compounds. The research was conducted over a period of three years. Experimental, numerical, and analytical studies were carried out. The experimental studies were conducted employing the counterflow configuration. Many hydrocarbon fuels and surrogates were tested. Critical conditions of extinction, critical conditions of autoignition and flame structures					
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## Report Title

### Autoignition and Combustion of JP-8 and its Surrogates at Moderate Pressures

#### ABSTRACT

The principal objective of the research is to develop surrogates that will reproduce selected aspects of combustion of JP-8 in laminar non-premixed and premixed flows. Surrogates are mixtures of hydrocarbon compounds. The research was conducted over a period of three years. Experimental, numerical, and analytical studies were carried out. The experimental studies were conducted employing the counterflow configuration. Many hydrocarbon fuels and surrogates were tested. Critical conditions of extinction, critical conditions of autoignition and flame structures were measured. It was found that the Aachen surrogate made up of 80% n-decane and 20% trimethylbenzene by weight, and surrogate C made up of 57% n-dodecane, 21% methylcyclohexane and 22% o-xylene by weight, reproduced key aspects of combustion of jet fuels in laminar premixed and nonpremixed flows. A key finding of this work was that low temperature chemistry plays an important role in promoting autoignition of high molecular weight hydrocarbon compounds. At low values of the strain rate the value of the autoignition temperature decreases with increasing molecular weight. An experimental facility was built for testing aspects of combustion at moderate pressures. Critical conditions of extinction were measured for hydrogen flames at pressures up to 1.5MPa.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

#### (a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
2011/08/31 0 7	Stefan Humer, Reinhard Seiser, and Kalyanasundaram Seshadri. Experimental Investigation of Combustion of Jet Fuels and Surrogates in Nonpremixed Flows, Journal of Propulsion and Power, (07 2011): 847. doi:
2011/08/30 1 6	S.M. Sarathy,, C.K. Westbrook,, M. Mehl,, W.J. Pitz,, C. Togbe,, P. Dagaut,, H. Wang,, M.A. Oehlschlaeger, , U. Niemann,, K. Seshadri, P.S. Veloo,, C. Ji,, F.N. Egolfopoulos,, T. Lu. Comprehensive chemical kinetic modeling of the oxidation of 2-methylalkanes from C7 to C20, Combustion and Flame, (06 2011): 0. doi: 10.1016/j.combustflame.2011.05.007
2011/08/30 1 5	Roberto Grana,, Kalyanasundaram Seshadri,, Alberto Cuoci,, Ulrich Niemann,, Tiziano Faravelli,, Eliseo Ranzi. Kinetic modelling of extinction and autoignition of condensed hydrocarbon fuels in non-premixed flows with comparison to experiment, Combustion and Flame, (08 2011): 0. doi: 10.1016/j.combustflame.2011.06.019
2011/08/30 1 4	Kalyanasundaram Seshadri,, Alessio Frassoldati,, Alberto Cuoci,, Tiziano Faravelli,, Ulrich Niemann,, Patrick Weydert,, Eliseo Ranzi. Experimental and kinetic modeling study of combustion of JP-8, its surrogates and components in laminar premixed flows, Combustion Theory Modelling, (08 2011): 569. doi: 10.1080/13647830.2011.552635
2011/08/30 1 3	Reinhard Seiser, Ulrich Niemann, Kalyanasundaram Seshadri. Experimental study of combustion of n-decane and JP-10 in non-premixed flows, Proceedings of the Combustion Institute, (01 2011): 1045. doi: 10.1016/j.proci.2010.06.078
2011/08/30 1 1	Ulrich Niemann, Reinhard Seiser and Kalyanasundaram Seshadri. Ignition and extinction of low molecular weight esters in nonpremixed flows, Combustion Theory Modelling, (12 2010): 875. doi:

**TOTAL: 6**

**Number of Papers published in peer-reviewed journals:**

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#### (b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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**(c) Presentations**

1. Humer, S., Niemann, U., Seiser, R., Seshadri, K., and Pucher, E., "Combustion of Jet Fuels and its Surrogates in Laminar Nonuniform Flows," Paper # 427, The 4th European Combustion Meeting, Vienna Institute of Technology, April 14–17, 2009.
2. Seshadri, K., Frassoldati, A., Cuoci, A., Faravelli, T., Niemann, U., Weydert, P., Ranzi, E., "Experimental and Kinetic Modeling Study of Combustion of JP-8, its Surrogates and Components in Laminar Premixed Flows," Paper # 10S-31, 2010 Spring Meeting, The Western States Section of the Combustion Institute, University of Colorado, Boulder, Colorado, 21-23 March 2010.
3. Seshadri, K., Frassoldati, A., Cuoci, A., Faravelli, T., Niemann, U., Weydert, P., Ranzi, E., "Experimental and Kinetic Modeling Study of Combustion of JP-8, its Surrogates and Components in Laminar Premixed Flows," Paper # 2C11, Twenty-Third International Symposium on Combustion, Tsinghua University, Beijing, China, 1-6 August 2010.
4. Grana, R., Niemann, U., Seshadri, K., and Ranzi, E., "Kinetic Modelling of Autoignition of Condensed Hydrocarbon Fuels in Nonpremixed Flows with Comparison to Experiment," 7th US National Technical Meeting of the Combustion Institute, Georgia Institute of Technology, Atlanta, GA, March 20-23, 2011.
5. Seshadri, K., "Simplified Chemical Kinetic Mechanisms with Application to Combustion," Keynote lecture, 22nd National Conference on I. C. Engines and Combustion, National Institute of Technology, Calicut, India, December 10-13, 2011.
6. Amin, V., Lee, J., Seiser, R., and Seshadri, K., "The Structure, Extinction, and Autoignition of Nonpremixed Toluene Flames," Paper # 12S-54, Spring Technical Meeting of the Western States Section of the Combustion Institute, Arizona State University, Tempe, AZ, March 19-20, 2012.

**Number of Presentations:** 6.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**(d) Manuscripts**

<u>Received</u>	<u>Paper</u>
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- |                 |   |
|-----------------|---|
| 2012/06/17 0: 9 | S.M. Sarathy, U. Niemann, C. Yeung, R. Gehmlich, C.K. Westbrook, M. Plomer, Z. Luo, M. Mehl, W.J. Pitz, K. Seshadri, M.J. Thomson, T. Lu. A counterflow diffusion flame study of lightly branched octane isomers, Proceedings of the Combustion Institute (01 2012) |
| 2012/06/17 0: 8 | Ulrich Niemann, Kalyanasundaram Seshadri, Forman A. Williams. Effect of Pressure on Structure and Extinction of Near-Limit Hydrogen Counterflow Diffusion Flames, Proceedings of the Combustion Institute (05 2012)   |

**TOTAL: 2**

Number of Manuscripts:

Books	
Received	Paper

TOTAL:

Patents Submitted

Patents Awarded	
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Awards	
None	

Graduate Students		
NAME	PERCENT SUPPORTED	Discipline
Ulrich Niemann	0.37	
Roberto Grana	0.01	
FTE Equivalent:	0.38	
Total Number:	2	

Names of Post Doctorates	
NAME	PERCENT SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported		
NAME	PERCENT SUPPORTED	National Academy Member
Kalyanasundaram Seshadri	0.09	
FTE Equivalent:	0.09	
Total Number:	1	

Names of Under Graduate students supported	
NAME	PERCENT SUPPORTED
FTE Equivalent:	
Total Number:	

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): ..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ..... 0.00

### Names of Personnel receiving masters degrees

NAME

Total Number:

### Names of personnel receiving PhDs

NAME

Total Number:

### Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

### Sub Contractors (DD882)

### Inventions (DD882)

## **Scientific Progress**

See Attachment

## **Technology Transfer**

# Autoignition and Combustion of JP-8 and its Surrogates at Moderate Pressures

## 1 Statement of the Problem Studied

The Department of Defense directive # 4140.25 dated April 12, 2004 mandates that “primary fuel support for land-based air and ground forces in all theaters (overseas and in the Continental United States) shall be accomplished using a single kerosene-based fuel, in order of precedence: JP-8, commercial jet fuel (with additive package), or commercial jet fuel (without additives).” A key challenge is to develop technologies for converting diesel-powered equipment employed by the US Army so that they can be powered by JP-8. This conversion is a complicated process. Many issues with fuel properties and performance have to be considered. They include autoignition, combustion, fuel injection, lubricity, and spray characteristics. Another application where conversion is required is unmanned aerial vehicles (UAV). Currently the UAVs in the field use gasoline or specialty fuels. The Army and other DOD services are in the process of developing technologies that would enable UAV’s to operate on JP-8. It is very likely that UAV’s will employ internal combustion engines that employ spark-ignition or compression-ignition.

JP-8 is a mixture of numerous aliphatic and aromatic compounds. The major components of this fuel are straight chain paraffins, branched chain paraffins, cycloparaffins, aromatics, and alkenes. The concentration of paraffins is on the average 60 % by volume, that of cycloparaffins 20 %, that of aromatics 18 %, and that of alkenes 2 %. It has been established that an useful approach is to first develop surrogates that reproduce selected aspects of combustion of JP-8. Surrogates are mixtures of hydrocarbon compounds. The hydrocarbon compounds used to construct the surrogate will depend on those aspects of combustion of JP-8 that the surrogate is expected to reproduce.

The research described in this report was carried out over a period of three years. Experimental and theoretical studies have been carried out. It was found that a surrogate made up of (80 % *n*-decane and 20 % and trimethylbenzene), called the Aachen surrogate accurately reproduces many aspects of combustion of JP-8. A “High Pressure Combustion Experimental Facility” (HPCEF) was constructed, using DURIP support from the U. S. Army Research Office for carrying out experiments at pressures up to 25 bar. This facility was used to study various aspects of combustion of gaseous fuels, for example methane, ethane and hydrogen. It

will be used in the future to study combustion of high molecular weight hydrocarbon fuels in laminar nonuniform flows. In the HPCEF different types of counterflow burners can be placed inside a high pressure chamber.

The following section is a summary of the most important results.

## 2 Summary of the Most Important Results

The research is described in the following eight archival publications.

1. Humer, S., Seiser, R., and Seshadri, K., “Experimental Investigation of Combustion of Jet Fuels and Surrogates in Nonpremixed Flows,” *Journal of Propulsion and Power*, **27**, 2011, pp 847—855.
2. Seshadri, K., Frassoldati, A., Cuoci, A., Faravelli, T., Niemann, U., Weydert, P., and Ranzi, E., “Experimental and Kinetic Modeling Study of Combustion of JP-8, its Surrogates and Components in Laminar Premixed Flows,” *Combustion Theory and Modelling*, **157**, 2011, pp 569—583.
3. Seiser, R., Niemann, U., and Seshadri, K., “Experimental Study of Combustion of *n*-Decane and JP-10 in non-premixed Flows,” *Proceedings of the Combustion Institute*, **33**, 2011, pp 1045—1052.
4. Niemann, U., Seiser, R., and Seshadri, K., “Ignition and Extinction of Low Molecular Weight Esters in Nonpremixed Flows,” *Combustion Theory and Modelling*, **14**, 2010, pp 875—891.
5. Sarathy, S. M., Westbrook, C. K., Mehl, M., Pitz, W. J., Togbe, C., Dagaut, P., Wang, W., Oehlschlaeger, M. A., Niemann, U., Seshadri, K., Veloo, P. S., Ji, C., Egolfopoulos, F. N., Lu, T., “Comprehensive Chemical Kinetic Modeling of the Oxidation of 2-Methylalkanes from C<sub>7</sub> to C<sub>20</sub>” *Combustion and Flame*, **158**, 2011, pp 2338—2357.
6. Grana, R., Seshadri, K., Cuoci, A., Niemann, U., Faravelli, T., and Ranzi, E., “Kinetic Modelling of Extinction and Autoignition of Condensed Hydrocarbon Fuels in Non-Premixed Flows with Comparison to Experiment,” *Combustion and Flame*, **159**, 2012, pp 130—141.



7. U. Niemann, K. Seshadri, F.A. Williams, "Effect of Pressure on Structure and Extinction of Near-Limit Hydrogen Counterflow Diffusion Flames," *Proceedings of the Combustion Institute*, **34**, 2012, in press
8. S. M. Sarathy, U. Niemann, C. Yeung, R. Gehmlich, C. K. Westbrook, M. Plomer, Z. Luo, M. Mehl, W. J. Pitz, K. Seshadri, M.J. Thomson, T. Lu, "A counterflow diffusion flame study of lightly branched octane isomers," *Proceedings of the Combustion Institute*, **34**, 2012, in press.

A brief description of the most important findings described in these publications are given below.

## 2.1 Experimental Investigation of Combustion of Jet Fuels and Surrogates in Nonpremixed Flows

Experimental studies were carried out to characterize non-premixed combustion of jet fuels and a number of its surrogates in laminar nonuniform flows. The counterflow configuration was employed. Critical conditions of extinction and autoignition were measured for JP-8, Jet-A, and Fisher Tropsch (FT) JP-8@. Thirteen surrogates of JP-8 and one surrogate of FT JP-8 were tested. It was found that critical conditions of extinction and autoignition of JP-8 and Jet-A were similar, while FT JP-8 was more reactive than JP-8 and Jet-A. Among the surrogates tested, surrogate H made up of *n*-decane (80 %) and 1,3,5-trimethylbenzene (20 %) by liquid volume, and surrogate C made up of *n*-dodecane (60 %), methylcyclohexane (20 %), and *o*-xylene (20 %) by liquid volume best reproduce extinction and autoignition characteristics of JP-8. Surrogate G made up of *n*-decane (60 %) and *iso*-octane (40 %) by liquid volume best reproduces the combustion characteristics of FT JP-8.

## 2.2 Experimental and Kinetic Modeling Study of Combustion of JP-8, its Surrogates and Components in Laminar Premixed Flows

Experimental and kinetic modeling studies were carried out to characterize premixed combustion of jet fuels, its surrogates, and reference components in laminar nonuniform flows. In previous studies supported by the U.S Army Research Office, it was established that the Aachen surrogate made up of 80 % *n*-decane and 20 % trimethylbenzene by weight, and surrogate C made up of 57 % *n*-dodecane, 21 % methylcyclohexane and 22 % *o*-xylene by weight, reproduce key aspects of combustion of jet fuels in laminar nonpremixed flows. Here, these surrogates and a jet fuel were tested in premixed, nonuniform flows. The counterflow con-

figuration was employed, and critical conditions of extinction were measured. In addition, the reference components tested were *n*-heptane, *n*-decane, *n*-dodecane, methylcyclohexane, trimethylbenzene, and *o*-xylene. Measured critical conditions of extinction of the Aachen surrogate and surrogate C were compared with those for the jet fuel. In general the alkanes *n*-heptane, *n*-decane, and *n*-dodecane, and methylcyclohexane were found to be more reactive than the aromatics *o*-xylene and trimethylbenzene. Flame structure and critical conditions of extinction were predicted for the reference components and the surrogates using a semi-detailed kinetic model. The predicted values were compared with experimental data. Sensitivity analysis shows that the lower reactivity of the aromatic species arises from the formation of resonantly stabilized radicals. These radicals were found to have a scavenging effect. The present study on premixed flows together with previous studies on nonpremixed flows show that the Aachen surrogate and surrogate C reproduce many aspects of premixed and nonpremixed combustion of jet fuels.

### 2.3 Experimental Study of Combustion of *n*-Decane and JP-10 in Non-premixed Flows

Experiments were conducted on *n*-decane and JP-10 flames, stabilized between two counter-flowing streams. The fuel stream was a mixture of prevaporized fuel and nitrogen, and the oxidizer stream was air. Critical conditions of extinction for *n*-decane and critical conditions of autoignition for both fuels were measured. Concentration profiles of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>O, CH<sub>4</sub>, and hydrocarbons from C<sub>2</sub> to C<sub>6</sub> were measured. The measurements were made by removing gas samples from the flame using a quartz microprobe and analyzing the samples using a gas chromatograph. Temperature profiles were measured using a thermocouple. Numerical calculations were performed using detailed kinetic models to predict the flame structure and to obtain values for extinction and autoignition. The predicted values of the critical conditions of extinction and autoignition agree well with experimental data. The predicted profiles and maximum mass fractions of the major species were found to agree with experimental data. There were, however, differences between the predicted and measured mass fraction of those species that have more than three carbon atoms. Comparison of combustion characteristics of *n*-decane and JP-10 show that the critical conditions of autoignition were nearly the same. In general the concentrations of saturated hydrocarbons in the *n*-decane flame were higher than those in the JP-10 flame.

## 2.4 Ignition and Extinction of Low Molecular Weight Esters in Nonpremixed Flows

An experimental and kinetic modeling study was carried out to characterize combustion of low molecular weight esters in nonpremixed, nonuniform flows. An improved understanding of the combustion characteristics of low molecular weight esters will provide insights on combustion of high molecular weight esters and biodiesel. The fuels tested were methyl butanoate, methyl crotonate, ethyl propionate, biodiesel, and diesel. Two types of configuration—the condensed fuel configuration and the prevaporized fuel configuration, were employed. The condensed fuel configuration was particularly useful for studies on those liquid fuels that have high boiling points, for example biodiesel and diesel, where prevaporization, without thermal breakdown of the fuel, was difficult to achieve. In the condensed fuel configuration, an oxidizer, made up of a mixture of oxygen and nitrogen, flows over the vaporizing surface of a pool of liquid fuel. A stagnation-point boundary layer flow was established over the surface of the liquid pool. The flame was stabilized in the boundary layer. In the prevaporized fuel configuration, the flame was established in the mixing layer formed between two streams. One stream was a mixture of oxygen and nitrogen and the other was a mixture of prevaporized fuel and nitrogen. Critical conditions of extinction and ignition were measured. The results show that the critical conditions of extinction of diesel and biodiesel were nearly the same. Experimental data show that in general flames burning the esters were more difficult to extinguish in comparison to those for biodiesel. At the same value of a characteristic flow time, the ignition temperature for biodiesel was lower than that for diesel. The ignition temperatures for biodiesel were lower than those for the methyl esters tested here. Critical conditions of extinction and ignition for methyl butanoate were calculated using a detailed chemical kinetic mechanism. The results agreed well with the experimental data. The asymptotic structure of methyl butanoate flame was found to be similar to that for many hydrocarbon flames. This will facilitate analytical modeling, of structures of ester flames, using rate-ratio asymptotic techniques, developed previously for hydrocarbon flames.

## 2.5 Comprehensive Chemical Kinetic Modeling of the Oxidation of 2-Methylalkanes from C<sub>7</sub> to C<sub>20</sub>

Conventional petroleum jet and diesel fuels, as well as alternative FischerTropsch (FT) fuels and hydrotreated renewable jet (HRJ) fuels, contain high molecular weight lightly branched alkanes (i.e., methylalkanes) and straight chain alkanes (*n*-alkanes). Improving the combustion of these fuels in practical applications requires a fundamental understanding of large hydro-

carbon combustion chemistry. This research project presents a detailed and reduced chemical kinetic mechanism for singly methylated iso-alkanes (i.e., 2-methylalkanes) ranging from C<sub>7</sub> to C<sub>20</sub>. The mechanism also includes an updated version of our previously published C<sub>8</sub>C<sub>16</sub> *n*-alkanes model. The complete detailed mechanism contains approximately 7200 species 31400 reactions. The proposed model was validated against new experimental data from a variety of fundamental combustion devices including premixed and non-premixed flames, perfectly stirred reactors and shock tubes. This new model was used to show how the presence of a methyl branch affects important combustion properties such as laminar flame propagation, ignition, and species formation.

## 2.6 Kinetic Modelling of Extinction and Autoignition of Condensed Hydrocarbon Fuels in Non-Premixed Flows with Comparison to Experiment

A semi-detailed chemical-kinetic mechanism was used to predict critical conditions of extinction and autoignition of condensed hydrocarbon fuels in nonpremixed flows. The mechanism includes reactions that describe “low temperature chemistry” as well as “high temperature chemistry” for many high molecular weight fuels. The fuels considered here were *n*-heptane, *n*-decane, *n*-dodecane, *n*-hexadecane, and *iso*-octane. The kinetic model was validated by comparing its predictions of critical conditions of extinction and autoignition for these fuels with experimental data obtained in a counterflow configuration where a steady laminar flow of an oxidizer was directed over the vaporizing surface of a condensed fuel. The residence time in this configuration was given by the strain rate. The kinetic model predicts that *n*-heptane was most difficult to extinguish followed by *n*-decane, *n*-dodecane, and *n*-hexadecane. This was in agreement with experimental data. Computations show that the influence of low temperature chemistry on critical conditions of extinction was small. The kinetic model predicts that at low strain rates *n*-hexadecane was most easy to ignite followed by *n*-dodecane, *n*-decane, and *n*-heptane. At high values of strain rate, *n*-heptane was more easy to ignite in comparison to *n*-decane. This was again in agreement with experimental data, including the “cross-over” in relative reactivities of *n*-heptane and *n*-decane. Sensitivity analysis shows that at low strain rates autoignition was promoted by low temperature chemistry for all fuels. At high strain rates, autoignition for *n*-heptane was promoted by high temperature chemistry, whilst low temperature chemistry continues to play a significant role in promoting autoignition for the other straight-chain hydrocarbon fuels. The “cross-over” in relative reactivities of *n*-heptane and *n*-decane was attributed to competition between the rates of low temperature chemistry, rates of high temperature chemistry, and rates of molecular transport for these fuels.

## 2.7 Effect of Pressure on Structure and Extinction of Near-Limit Hydrogen Counterflow Diffusion Flames

Results of measurements of critical conditions for extinction and of temperature profiles in counterflow diffusion flames were reported. The fuel was a hydrogen-nitrogen mixture with 14 mole percent hydrogen, and the oxidizer was air. Pressures ranged from 0.1 MPa to 1.5 MPa; measurements were made in a facility especially constructed for carrying out counterflow combustion experiments at high pressures. With increasing pressure, the strain rate at extinction first increases and then decreases, in qualitative agreement with predictions, but there were observable quantitative differences. Temperature profiles, obtained employing an R-type thermocouple at a fixed strain rate of  $100\text{s}^{-1}$ , agree well with predictions, within experimental uncertainty. The results may help to improve knowledge of underlying chemical-kinetic and transport parameters at elevated pressures.

## 2.8 A Counterflow Diffusion Flame Study of lightly Branched Octane Isomers

Conventional petroleum, Fischer-Tropsch (FT), and other alternative hydrocarbon fuels typically contain a high concentration of lightly methylated *iso*-alkanes. However, until recently little work has been done on this important class of hydrocarbon components. In order to better understand the combustion characteristics of real fuels, this study presents new experimental data for 3-methylheptane and 2,5-dimethylhexane in counterflow diffusion flames. This new dataset includes flame ignition, extinction, and speciation profiles. The high temperature oxidation of these fuels has been modeled using an extended transport database and a high temperature skeletal chemical kinetic model. The skeletal model was generated from a detailed model reduced using the directed relation graph with expert knowledge (DRG-X) methodology. The proposed skeletal model contains sufficient chemical fidelity to accurately predict the experimental speciation data in flames. The predictions were compared to elucidate the effects of number and location of the methyl substitutions. The location was found to have little effect on ignition and extinction in these counterflow diffusion flames. However, increasing the number of methyl substitutions was found to inhibit ignition and promote extinction. Chemical kinetic modelling simulations were used to correlate a fuels extinction propensity with its ability to populate the H radical concentration. With regards to the species composition of these counterflow flames, the location and number of methyl substitutions was found to particularly affect the amount and type of alkenes observed.